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2D black phosphorous nanosheets as a hole transporting material in perovskite solar cells

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HIGHLIGHTS

- 2D Black Phosphorus has been used as a hole transporter in perovskite solar cells.
- Liquid phase exfoliated black phosphorus is extensively characterized.
- Efficient hole injection from perovskite into black phosphorus is shown.

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ABSTRACT

We demonstrate for the first-time liquid exfoliated few layers of 2D Black phosphorus (BP) nanosheets as a hole transporting material (HTM) for perovskite based solar cells. The photoelectron spectroscopy in air (PESA) measurements confirm the low laying valence band level of BP nanosheets (−5.2 eV) favourable for hole injection from $CH_3NH_3PbI_3$ ($MAPbI_3$). Our results show that ~25% improvement in power conversion efficiency (PCE) of $\eta = 16.4\%$ for BP nanosheets + Spiro-OMeTAD as an HTM as compared to spiro-OMeTAD ($\eta = 13.1\%$). When BP nanosheets are exclusively utilised as an HTM, a PCE of $\eta = 7.88\%$ is noted, an improvement over the 4% PCE values observed for HTM free devices. Photoluminescence (PL) quenching of $MAPbI_3$ and impedance measurements further confirm the charge extraction ability of BP nanosheets. The structural and optical characterization of liquid exfoliated BP nanosheets is discussed in detail with the aid of transmission electron microscopy, Raman spectroscopy, absorption spectroscopy and photo-electron spectroscopy.

1. Introduction

Organic–inorganic metal halide perovskite based solar cells, (with the general formula of ABX_3, where A is an organic cation, B is commonly Pb^{2+}, and X is a halide) have attracted extensive attention of photovoltaic researchers due to their immense progress in device performance from 3.8% to 22.1% [1–4]. Hybrid organic-inorganic perovskite materials have excellent photovoltaic properties such as high absorption coefficient, tunable band gaps and long electron–hole diffusion lengths [1,5–10].

Typically, in a perovskite solar cell, the perovskite absorbing layer is sandwiched between an electron transporting material (ETM) and a hole transporting material (HTM). The ETMs are either compact metal oxides (e.g TiO_2/ZnO/SnO_2 etc) or organic materials (fullerene (C_{60}) and phenyl-C_{61}-butyric acid methyl ester (PCBM)) while HTMs are organic, inorganic or polymeric materials [3,11–14]. Spiro-OMeTAD (2,2′,7,7′-Tetrakis-(N,N-di-*p*-methoxyphenylamine)-9, 9′-spirobiflorene) and PTAA (Poly (triarylamine) are the two commonly used HTMs in perovskite solar cells [15,16] and have played a crucial role in achieving high cell performance. However, the high costs, thermal and chemical instability of these materials hinder the viable commercialization of perovskite solar cells. Hence there is a need for alternative HTMs with low cost while still maintaining

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high efficiency. The key criteria for the selection of HTMs in perovskite solar cell is that the energy level of the valence band maximum (highest occupied molecular orbital (HOMO)) of HTM should be lower than that of the perovskite with suitable hole mobility and good thermal stability [17].

Recently, a number of two-dimensional (2D) materials including transition metal dichalcogenides (TMDs) have been proposed as potential candidates in electronics and optoelectronics due to their excellent tunable opto-electronic properties and their high carrier mobility with ambipolar characteristics [18–25]. However, these 2D semiconducting materials are prepared either by micromechanical exfoliation (which has ultra-low yield) or CVD approach which is a laborious and expensive technique. Further, reduced graphene oxide and graphene oxide are employed as hole conductor in perovskite solar cells and organic solar cells [25–28]. However, the graphene oxide possesses intrinsic disadvantages for HTMs such as an insulating nature and a high degree of oxygen content.

Black phosphorous (called as phosphorene in monolayer) is emerging as a promising 2D nanomaterial due to its suitable electronic and optoelectronic properties [29]. It is a van der Waals-bonded layered material with carrier mobility up to ~1000 $cm^2/V.s$ at room temperature (RT) [30,31]. BP exhibits layer dependent direct band gap ranging from ~0.3 eV (bulk) to ~2 eV (monolayer) and has received remarkable attention since its direct band gap nature is independent of layer number. Recently, the viability of phosphorene as a buffer layer for perovskite based solar cells has also been demonstrated [32,33]. The high optical transparency, good charge carrier mobility and extraordinary electronic properties at low costs open the possibility of it being employed as an HTM. However, the use of BP as an HTM has not been explored yet.

Here, we have validated liquid exfoliated few layers of 2D BP (BP nanosheets) as a potential buffer as well as an HTM layer for perovskite based solar cells. These BP nanosheets are further characterized by electron microscopy, Raman spectroscopy, absorption spectroscopy and photo-electron spectroscopy to confirm its structure and energy levels. Surprisingly, the improved power conversion efficiency (PCE) of $\eta = 16.4\%$ have been achieved for perovskite based solar cells employing BP nanosheets + Spiro-OMeTAD as an HTM as compared to spiro-OMeTAD ($\eta = 13.1\%$). Furthermore, thin films of BP nanosheets are incorporated as a hole transporting material (HTM) in multi-layered perovskite solar cell. A power conversion efficiency of $\eta = 7.8\%$ is achieved ($J_{sc} = 17.0$ mA/cm^2, Voc 0.84 V and FF = 54.7%) using BP nanosheets as an HTM. The effect of BP nanosheets on perovskite layer is corroborated by effective PL quenching at the perovskite-BP interface indicating efficient charge transfer. Furthermore, Electrochemical Impedance spectroscopy (EIS) measurements were also carried out at different applied bias to understand the charge transport properties of HTM. Our results indicate that solvent processed inorganic BP nanosheets as a potential HTM that can replace the conventional organic HTMs in perovskite based solar cells.

2. Results and discussion

Liquid phase exfoliation (LPE) process was employed to exfoliate few layers of black phosphorus (BP) nanosheets from bulk BP crystals (as purchased) in anhydrous N-methyl pyrrolidone (NMP) solvent using probe sonication method [34]. LPE is appropriate for the large-scale production of black phosphorus and proven for other 2D nanomaterials also [35]. The size and the concentration of exfoliated BP nanosheets in NMP were controlled by tuning the exfoliation and centrifugation isolation procedures. The morphology and characterizations of as exfoliated BP nanosheets are shown in Fig. 1. Field emission scanning electron microscopy image (Fig. 1a) confirms that BP nanosheets are randomly oriented with dense packing (Fig. 1a). High magnification image of BP nanosheet (Fig. 1b) indicates the atomically thin nature of BP nanosheet on holey carbon grid.

The lateral size distribution histogram of exfoliated BP nanosheets is shown in Fig. 1c, which reveals the average length of BP nanosheets (~100 nanosheets measured) is $< L > 1114 \pm 63$ nm. The high resolution transmission electron microscopy (HRTEM) image of the BP nanosheets (Fig. 1d and e) shows a lattice spacing of ~0.3 nm which corresponds to that of the (021) crystal planes [36,37]. The corresponding selected area electron diffraction (SAED) pattern consists of discrete spots indicating the high crystallinity of exfoliated BP nanosheets (inset in Fig. 1d). Raman spectroscopy was performed on drop casted BP nanosheets to confirm the characteristic peaks of the exfoliated sample. A typical Raman spectrum of few layered BP nanosheets reveals signatures of one out-of-plane A_g^1 (356 cm^{-1}) and two in-plane B_{2g} (429 cm^{-1}) and A_g^2 (457 cm^{-1}) phonon vibrational modes which are in good accordance with previous observations for BP [38] (Fig. 1f). To further clarify the valence states of exfoliated BP nanosheets, we acquired X-ray photoelectron spectroscopy (XPS) data with monochromatic Al Kα radiation ($h\nu = 1486.7$ eV). The wide-scan survey spectrum (shown in Fig. S1a) only shows the presence of O 1s, C 1s, and doublet P 2p signals. Fig. S1b shows the high resolution XPS of BP nanosheets, where $2p_{3/2}$ and $2p_{1/2}$ doublet at 129.5 and 130.3 eV, respectively, characteristic of elemental phosphorus [34]. Small oxidized phosphorus (i.e., P_xO_y) sub-bands at higher energy region around 133.8 eV is observed, an indication of the minor oxidation of BP nanosheets which is a fundamental stability issue with BP [34].

The exfoliated BP nanosheets were further used as HTM in perovskite based solar cells. Subsequently, in order to find the valence band position of exfoliated BP nanosheets, photoelectron spectroscopy in air (PESA) measurements have been carried out by preparing uniform thin film of BP nanosheets at optimized concentrations (BP/IPA suspension ~6 mg/ml) on ITO substrate. The cross over point is identified as ionization potential or valence band maximum obtained from PESA measurement which is 5.2 eV (Fig. 2a). This indicates that valence band position of the BP nanosheets is at lower energy level than the perovskite valence band (−5.4 eV), which provides the driving force for hole injection from the perovskite layer to BP nanosheets (Fig. 2b). The valence band energy level of BP nanosheets is fairly matching with commonly used organic hole-transporting material spiro-OMeTAD [15] in perovskite based devices. The conduction band energy level (−3.4 eV) was calculated by addition of band gap value (1.8 eV) to the valence band level (−5.2 eV). The band gap of BP (1.8 eV) was calculated from UV-Vis absorption measurements of BP nanosheets by using Tauc plot as shown below Fig. S2. After assessing the energy levels of BP nanosheets, we have fabricated solar cell devices using conventional architecture as depicted in Fig. 2d. The details of device fabrication are provided in experimental section. Concisely, the device structure consists of FTO/BL TiO_2/mesoporous TiO_2/$MAPbI_3$/BP nanosheet film/Au. Blocking layer of TiO_2 layer was deposited by spray pyrolysis method on FTO glass, followed by mesoporous TiO_2 layer (~300 nm). Then, $MAPbI_3$ was deposited using single step deposition method. The BP nanosheets dispersed in isopropyl alcohol (IPA) with appropriate concentration (~6 mg/ml in anhydrous IPA solvent) was spin coated on perovskite layer followed by the Au electrode evaporation (~110 nm). The concentration of the BP nanosheet in IPA is optimized based on the preliminary experiments in order to achieve the maximum surface coverage on the perovskite in order to minimise shunting at the perovskite-Au interface. The obtained device data is compared with that of the most commonly used organic HTM i.e spiro-OMeTAD. Fig. 2c exhibits the characteristic current density (J_{sc}) vs voltage (V) curve of the best performing perovskite based device using BP nanosheets as HTM.

The obtained power conversion efficiency (PCE) is 7.88% with open circuit potential (V_{OC}) of 0.84 V, current density (J_{SC}) of 17.0 mA/cm^2, and fill factor (FF) of 0.54 under one sun illumination (AM1.5 100 mW/cm^2). The reference devices were also fabricated under similar experimental conditions using the conventional spiro-OMeTAD as an HTM with device architecture consists of: I) FTO/BL TiO_2/mesoporousTiO_2/$MAPbI_3$/spiro-OMeTAD/Au, ii) without HTM i.e.FTO/BL TiO_2/